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Original Research Paper

Facile and green synthesis of highly dispersed cobalt oxide (Co_3O_4) nano powder: Characterization and screening of its eco-toxicity

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ABSTRACT

A novel green synthesis of cobalt oxide (Co_3O_4) nanoparticles using latex of *Calotropis procera* via simple precipitation method at room temperature was investigated. An extensive characterization of the product was carried out using X-ray diffractometry (XRD), Differential scanning calorimetry (DSC), Transmission electron microscopy (TEM), Energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and UV–Visible spectroscopy. The results of the characterization confirmed that the synthesized nanomaterial is highly dispersed. TEM analysis revealed that the nano particles are having an average size around 10 nm. The eco-toxic investigation suggested that the particles are non-toxic and safe towards the environment. This green strategy proves to be an effective, fast, simple and cost-effective approach for the synthesis of Co_3O_4 nanoparticles for various applications.

1. Introduction

Among numerous transition metal oxides that have been extensively investigated due to their intriguing electronic, electrical, catalytic and magnetic properties and wide range applications in almost every branch of science and technology, cobalt oxide (Co_3O_4) nanoparticles having normal spinel structure have been widely explored and considered as promising types of multifunctional materials due to their extensive applications in lithium-ion batteries [1–3], magnetic semiconductors [4,5], gas-sensing, heterogeneous catalysis [6–8] and electro-chromic devices, field-emission materials, solar energy storage and pigments, and super-capacitors [9–13]. Belonging to the normal spinel and monoclinic crystal structure, cobalt oxide (Co_3O_4) nanoparticles possess cubic close packed array of oxide ions in which Co(II) ions occupy the tetrahedral 8a sites whereas, Co(III) ions fit into the octahedral 16d sites [14].

Several methods such as co-precipitation, sol-gel, sonochemical route, chemical-vapor deposition, and thermal decomposition of cobalt-precursors [15–21] have been reported for the synthesis of these nanoparticles. Hydrothermal method, chemical spray pyrolysis, combustion method, mechano-chemical processing, microwave irradiation, and micro-emulsion methods [22–27] have also been devised for the synthesis of Co_3O_4 nanoparticles of different morphologies. However, most of these synthesis routes have been associated with a number of drawbacks to the use of expensive equipments, complex synthesis steps, high temperature, prolonged reaction time, and a high cost of synthesis. Also, none of the above methods are environmentally benign.

Materials reduced to nano-dimension possesses a multiplicity of unique physical and chemical properties compared to their bulk counterparts mainly due to surface and volume effects [28]. Surface effect is held responsible for the high chemical activity of the nanomaterials while the enhanced catalytic properties of the nanomaterials are explained by volume effects. Despite of the various fascinating properties possessed by nanoparticles, the most unavoidable problem associated with the particles of nanometer range is their intrinsic instability. The nanoparticles are more prone to agglomerate to reduce the energy associated with the higher surface area to volume ratio. Thus, to stabilize nano-sized particles and uphold their corresponding property strategies must be contrived to prevent their self-aggregation. In this aspect, the addition of certain organic solvents, reducing agents and surface active agents (surfactants) that prevent agglomeration and results into dispersed particles has been emphasized. However, being highly toxic and reactive, these chemicals pose potential environmental and biological risks. Hence, an alternative approach for minimization or elimination of such kinds of toxic chemicals and use of environmentally benign materials during the synthesis pro-

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tocol is offered by green chemistry. Since last two decades, green chemistry has been acknowledged as an innovative tool for the reduction in the application of toxic and hazardous chemicals utilized during nanoparticle synthesis protocol in both research and industry. It involves the use of environmentally benign materials that offers numerous benefits in terms of eco-friendliness and compatibility. Therefore, several green approaches have been adopted to minimize the use of certain chemicals (capping agents, reducing agents, and solvent) utilized during synthesis of various nanoparticles [29–39]. Of various green strategies devised for synthesis of nanoparticles, biosynthesis using plants is considered to be safe, economically viable and eco-friendly approach that lead to the formation of stable nanoparticles at a faster rate [32]. The literature survey on the green synthesis of Co_3O_4 nanoparticles revealed that these particles are synthesized via different plant extracts such as leaves extract of *Calotropis gigantea* [40] and *Aspalathus linearis* [41], peal extract of *Punica granatum* [42], etc. The lack of any report on the green synthesis of Co_3O_4 nanoparticles using latex of the plant, *Calotropis procera* encouraged us to use it as a surface stabilizing agent during Co_3O_4 nanoparticles synthesis. The present study focuses on the green synthesis of monodispersed Co_3O_4 nanoparticles by bio-component of latex obtained through plant of *Calotropis procera*.

The plant *Calotropis procera* belonging to the family Asclepiadaceae also called as Alarka, Mandara, Shwetarka, Vasuka, is a xerophytic shrub distributed throughout India. The different parts of the plant are known to be used in Indian traditional medicine for the treatment of painful muscular spasm, dysentery, fever, rheumatism, asthma and as an expectorant and purgative. The plant is also known for its anti-cancer, antifungal and insecticidal activity. The flowers exhibits hepatoprotective an larvicidal activities, antipyretic, anti-inflammatory, analgesic and antimicrobial effects, the roots shows anti-ulcer and antifertility effects, and the latex of the plants possess wound healing, analgesic, anti-inflammatory and antimicrobial activities [43]. The chemical composition of crude latex shows that more than 80% of its dry mass corresponds to the rubber and remaining 20% contains various soluble biologically active compounds rich in carbohydrates, proteins, amino acids, vitamins, lipids, anti-oxidants enzymes, tryptophan, alkaloids, resins, and tannins, etc. [44]. Furthermore, it is known to have predominantly the alkaloids namely calotropin, calactin, and calotoxin [45]. However, its main constituent is reported to be rubber, which is highly insoluble in water [46].

To the best of our consent, a green approach using bio-component of the latex of *Calotropis procera* has been used for the first time as a surface stabilizing agent for the fabrication of highly dispersed, nearly spherical-shaped cobalt oxide nanoparticles. The structure, phase, and morphology of synthesized product were investigated by various standard analytical characterization techniques. Besides physical characterization, eco-toxicity of the synthesized Co_3O_4–NPs has further been investigated. In the present communication, a bio-component assisted green synthesis strategy has been successfully developed to prepare spherical Co_3O_4 nanoparticles for the first time.

2. Experimental details

2.1. Materials

All reagents viz., cobalt acetate tetrahydrate [$Co(CH_3COO)_2{\cdot}4H_2O$] and 25% ammonia solution ($NH_3{\cdot}H_2O$) were procured from MERCK and were used without any further purification and latex derived from the fresh leaves of *Calotropis procera* was used without any further treatment.

2.2. Collection of latex

The fresh milky latex was collected from the leaves of healthy plants of *Calotropis procera* from the local ground and kept in the refrigerator at 4 °C for further use.

2.3. Sample preparation

Nano-cobalt or cobaltic oxide was synthesized via precipitation method and the typical synthesis involved a homogeneous 0.4 M aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ obtained by mixing its proper amount into distilled water with a vigorous stirring. Thereafter, a known amount of latex was added into the above mixture with stirring for approximately 10 min. The solution of $Co(CH_3COO)_2$ was then precipitated by $NH_3{\cdot}H_2O$ (25%) under vigorous mechanical stirring at a constant agitation speed. The resulting solution mixture was kept for continuous magnetic stirring for about 2 h. The dark green precipitate of $Co(OH)_2$ thus obtained was washed repeatedly with distilled water and finally with ethanol to remove any impurity adhered on its surface. After multistep washings, the solid mass was dried at 60 °C in a hot air oven for 24 h and the obtained solid product was crushed and sieved to get uniform particle size. Afterwards, the powdered material was annealed at 450 °C for 3 h at a steady heating rate of 12 °C min^{-1} to produce black colored nano-sized cobalt oxide which was further sieved through 65 μm sieve and then stored for characterization.

Extensive characterization of the synthesized material was carried out by Powder X-ray Diffractometer (RIGAKU MINIFLEX II, Desktop XRD), Fourier Transform Infrared Spectroscopy (JASCO-FTIR Spectrometer and ALPHA-FTIR Spectrometer), Scanning Electron Microscopy (QUANTA 200 F), Energy Dispersive X-ray (EDX) spectrometer (Kevex Sigma Energy Dispersive X-ray Analysis System Level KS-2), Transmission Electron Microscopy (Technai20-G^2 FEI, Holland), BET Surface area analyzer (computer controlled automated porosimeter (Micromeritics ASAP 2020, V3.02G single port)), Differential Scanning Calorimetry (TC 15 TA Controller MettlerTole Do.) and UV–Visible Spectroscopy (UV-1700 Pharmaspec spectrometer).

2.4. Test of eco-toxicity

Eco-toxicity in terms of the antibacterial activity of Co_3O_4-NPs was tested on three gram-negative (*E. coli, Pseudomonas* sp., *and Alcaligenes* sp.) and one gram-positive bacterium (*Enterococcus* sp.) by the disc diffusion technique using Kirby-Bauer method [47]. All these bacteria were isolated from diabetic foot ulcers of patients admitted to Sir Sundarlal Hospital, Banaras Hindu University, Varanasi. Identification of all the isolates was made by 16S rRNA gene sequencing. Cultures were routinely grown in Luria Bertani (LB) medium in a bacteriological incubator at 37 °C for 24 h. The antibacterial effect of Co_3O_4-NPs was tested at concentrations of 100–750 μg/disc in Petri plates containing solid LB agar medium. Inoculum (100 μl) of each bacterial strain was uniformly spread on solid LB agar medium and then sterilized paper discs (5 mm diameter) loaded with 100, 250, 500 and 750 μg/disc of Co_3O_4-NPs were carefully placed in each plate. For the negative control, paper discs with sterile 0.1 N NaOH or the latex of *C. procera* were placed over the bacterial lawn in different plates. Ampicillin was used as positive control at the concentration used for Co_3O_4-NPs. For loading of Co_3O_4-NPs onto paper discs, solution of Co_3O_4-NPs was prepared in 0.1 N NaOH with desired stock concentration and thereafter 10 μl of each was loaded on paper disc by glass micro-capillary pipette following the steps used in loading of the samples in paper/thin layer chromatography. The paper discs were dried and sterilized before placing on agar plates. The development of clear zone

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